the wavelengths of visible light spectrum and therefore can induce higher haze (i.e., > 4%) to reduce display quality.

SUMMARY

[0009] A subwavelength structured surface gradient solution is therefore desired. Preferably, the solution provides a relatively low reflection (i.e., average reflection over the visible range less than, less than 2.0 (in some embodiments, less than 1.5, or even less than 1.0) percent) and durable characteristics to enhance the viewing quality of display devices.

[0010] In one aspect, the present disclosure describes a material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, the first region having the outer major surface wherein at least the outer most sub micrometer particles are partially conformally coated by (and optionally covalently bonded to) the polymeric matrix, wherein the first and second regions have first and second average densities, respectively, and wherein the first average density is less than the average second density. In some embodiments, the difference between the first and second average densities is in a range from 0.1 g/cm3 to 0.8 g/cm3 (in some embodiments, 0.2 g/cm3 to 0.7g/cm3, or even 0.3 g/cm3 to 0.6 g/cm3). In some embodiments, the second region is substantially free of closed porosity (i.e., free of than closed pores greater than 200 nm (in some embodiments, greater than 150 nm, 100 nm, or even greater than 50 nm) in diameter). In some embodiments, the sub-micrometer particles each have an outer surface, and wherein at least 50 (in some embodiments, at least 60, 70, 75, 80, 90, 95, 99, or even 100) percent by volume of the sub-micrometer particles have their outer surface is free of fluorine. In some embodiments, the material having a Steel Wool Scratch Test value of at least 1 (in some embodiments, of at least 2, 3, 4, or even 5). In some embodiments, the sub-micrometer particles dispersed in the polymeric matrix has an average particle size, and the first region has a thickness less than (in some embodiments equal to; in some embodiments, greater than; in some embodiments, at least twice; in some embodiments three to five times) the average particle size of the sub-micrometer particles.

[0011] ~~In another aspect, t~~The present disclosure describes a material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, wherein the first and second regions have first and second densities, respectively, and wherein the first average density is less than the second average density, and wherein the material having a Steel Wool Scratch Test value of at least 1 (in some embodiments, of at least 2, 3, 4, or 5). In another aspect, the present disclosure describes a material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, wherein the first and second regions have first and second densities, respectively, wherein the first average density is less than the second average density, wherein the first region having an outer major surface, wherein at least the outer most sub-micrometer particles are partially conformally coated with the polymeric matrix, and wherein the material having a Steel Wool Scratch Test value of at least 1. In some embodiments, the first region having the outer major surface wherein at least the outer most sub-micrometer particles are partially conformally coated with the polymeric matrix. In some embodiments, the sub-micrometer particles are covalently bonded to the polymeric matrix. In some embodiments, the second region is substantially free of

closed porosity. In some embodiments, the sub micrometer particles each have an outer surface, and wherein at least 50 (in some embodiments, at least 60, 70, 75, 80, 90, 95, 99, or even 100) percent by volume of the sub micrometer particles have their outer surface is free of fluorine. In some embodiments, the sub micrometer particles dispersed in the

21. The method of claim 20, wherein the first inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm, and wherein the second inhibitor gas has an oxygen content in a range from 100 ppm to100,000 ppm.

22. The method of either claim 20 or 21, wherein final curing of the free radical curable layer is conducted in the second chamber.

23. The method of any one of claims 17 to 22, wherein a portion of the actinic radiation curing is conducted in a first chamber having a first inhibitor gas and a first actinic radiation level, and a portion of the actinic radiation curing is conducted in a second chamber having a second inhibitor gas and a second actinic radiation level, wherein the first inhibitor gas has a higher oxygen content than the second inhibitor gas, and wherein the first actinic radiation level is lower than the second actinic radiation level.

24. The method of claim 23, wherein the first inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm, and wherein the second inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm.

25. The method of either claim 23 or 24, wherein final curing of the free radical curable layer is conducted in the second chamber.

26. A material comprising sub-micrometer particles dispersed in a polymeric matrix, the material having a thickness, at least first and second integral regions across the thickness, wherein the first and second regions have first and second average densities, respectively, ~~and~~ wherein the first average density is less than the second average density, wherein the first region having an outer major surface, wherein at least the outer most sub-micrometer particles are partially conformally coated with the polymeric matrix, and wherein the material has a Steel Wool Scratch Test value of at least 1.

~~27. The material of claim 26, the first region having the outer major surface wherein at least the outer most sub-micrometer particles are partially conformally coated with the polymeric matrix.~~

~~28~~27. The material of ~~either~~ claim 26 ~~or 27~~, wherein the sub-micrometer particles are covalently bonded to the polymeric matrix.

~~29~~28. The material of ~~any one of~~either claims 26 ~~to 28~~or 27, wherein, the difference between the first and second average densities is in a range from 0.1 g/cm^3 to 0.8 g/cm^3.

~~30~~29. The material of any one of claims 26 to ~~29~~28, wherein the second region is free of substantially closed porosity.

~~31~~30. The material of any one of claims 26 to ~~30~~29, wherein at least a portion of the polymer is made from a prepolymer comprising free radically curable prepolymer.

~~32~~31. The material of claim ~~31~~30, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric multifunctional (meth)acrylate.

~~33~~32. The material of claim ~~31~~30, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric difunctional (meth)acrylate.

~~34~~33. The material of claim ~~31~~30, wherein at least a portion of the prepolymer comprises at least one of a monomeric or oligomeric monofunctional (meth)acrylate.

~~35~~34. The material of claim ~~34~~33, wherein at least a portion of the prepolymer comprises a mixture of mutifuctional, difuctional, and monofunction (meth)acrylates.

~~36~~35. The material of any one of claims ~~31~~30 to ~~35~~34, wherein the prepolymer composition has a functionality of 1.25 to 2.75.

~~37~~36. The material of any of claim 26 to ~~36~~35, wherein the sub-micrometer particles comprise surface modified sub-micrometer particles.

~~38~~37. The material of any one of claims 26 to ~~37~~36, wherein the sub-micrometer particles have particle sizes of at least 5 nm to 1000 nm.

~~39~~38. The material of any one of claims 26 to ~~38~~37, wherein the sub-micrometer particles comprise silica.

~~40~~39. The material of any one of claims 26 to ~~39~~38, wherein the sub-micrometer particles have sub-micrometer particle sizes in a range from 5 nm to 10 micrometer.

~~41~~40. The material of any one of claims 26 to ~~40~~39, wherein there is an average spacing between the protruding sub-micrometer particles in a range from 40 nm to 300 nm.

4241. The material of any one of claims 26 to 4140, wherein the material further comprises an outer layer comprising agglomerates of silica nanoparticles, the silica nanoparticles having an average particle diameter of 40 nanometers or less, said agglomerates comprising a three-dimensional porous network of silica nanoparticles, further wherein the silica nanoparticles are bonded to adjacent silica nanoparticles.

4342. A method of making a material of any one of claims 26 to 4241, the method comprising:

providing a free radical curable layer having sub-micrometer particles dispersed therein; and

actinic radiation curing the free radical curable layer in the presence of a sufficient amount of inhibitor gas, to inhibit the curing of a major surface region of the layer to provide a layer having a bulk region with a first degree of cure and a major surface region having a second degree of cure, wherein the first degree of cure is greater than the second degree of cure, and wherein the material having a structured surface that includes a portion of the sub-micrometer particles.

4443. The method of claim 4342, wherein the inhibiting gas has an oxygen content is 100 ppm to 100,000 ppm.

4544. The method of either claim 43-42 or 4443, wherein all actinic radiation curing is conducted in a single chamber.

4645. The method of any one of claims 43-42 to 4544, wherein a portion of the actinic radiation curing is conducted in a first chamber having a first inhibitor gas and a first actinic radiation level, and a portion of the actinic radiation curing is conducted in a second chamber having a second inhibitor gas and a second actinic radiation level, wherein the first inhibitor gas has a lower oxygen content than the second inhibitor gas, and wherein the first actinic radiation level is higher than the second actinic radiation level.

4746. The method of claim 4645, wherein the first inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm, and wherein the second inhibitor gas has an oxygen content in a range from 100 ppm to100,000 ppm.

4847. The method of either claim 46-45 or 4746, wherein final curing of the free radical curable layer is conducted in the second chamber.

4948. The method of any one of claims 43-42 to 4847, wherein a portion of the actinic radiation curing is conducted in a first chamber having a first inhibitor gas and a first actinic radiation level, and a

portion of the actinic radiation curing is conducted in a second chamber having a second inhibitor gas and a second actinic radiation level, wherein the first inhibitor gas has a higher oxygen content than the second inhibitor gas, and wherein the first actinic radiation level is lower than the second actinic radiation level.

~~50~~49. The method of claim ~~49~~48, wherein the first inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm, and wherein the second inhibitor gas has an oxygen content in a range from 100 ppm to 100,000 ppm.

~~51~~50. The method of either claim ~~49~~48 or ~~50~~49, wherein final curing of the free radical curable layer is conducted in the second chamber.

~~52~~51. The method of any one of claims 17 to 25 or ~~43~~42 to ~~51~~50, further comprising contacting the layer with a coating composition comprising: a) 0.5 to 99 wt. % water b) 0.1 to 20 wt. % silica nanoparticles having an average particle diameter of 40 nm or less, c) 0 to 20 wt. % silica nanoparticles having an average particle diameter of 50 nm or more, wherein the sum of b) and c) is 0.1 to 20 wt. %; d) a sufficient amount of an acid having a pKa of < 3.5 to reduce the pH to less than 5; e) 0 to 20 percent by weight of a tetraalkoxysilane, relative to the amount of the silica nanoparticle; and

drying to provide a silica nanoparticle coating on the layer.

~~53~~52. A nanostructured material made according to the method of claim ~~52~~51.